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Extraction of Rhodium(III) from Hydrochloric Acid Solutions with Bis-Acylated Triethylenetetramine Dihydrochloride

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Abstract—Extraction of rhodium(III) from hydrochloric acid solutions with bisacylated triethylenetetramine dihydrochloride has been studied. The optimal extraction conditions have been elaborated. At the phase contact time of 5 min rhodium(III) is extracted via the interphase anionic exchange mechanism. Concentration constants of extraction have been calculated, and thermodynamic parameters of extraction have been estimated. The extracted ion associate has been isolated and characterized by means of electronic, IR, and ^{13}C NMR spectroscopy.

Keywords: rhodium(III), extraction, hydrochloric acid solutions, bisacylated triethylenetetramine, dihydrochloride

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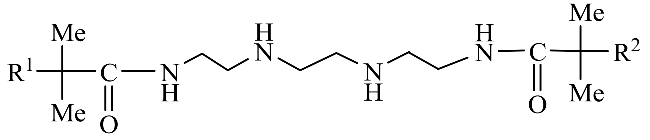
At the final stage of separation of the platinum group elements via the conventional extraction scheme rhodium(III) is retained in the aqueous solution [1–4]. Extraction of rhodium from such solutions of complex composition is a topical issue; the solutions proposed so far include extraction with Alamine 336, Kelex 100 [5–7], or TBP in the presence of tin(II) chloride [8]. The inefficient extraction of rhodium(III) at its relatively high concentration is a common drawback of these methods, whereas in the latter case separation of rhodium(III) from the multi-fold excess of tin(II) additionally complicate the process. In an attempt to resolved the above-mentioned issues, in this work we studied extraction of rhodium(III) from hydrochloric acid solutions with bisacylated triethylenetetramine dihydrochloride.



R^1, R^2 = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$.

The used reagent is a high-boiling mixture of the homologs (average M = 480) [9]. We have earlier demonstrated that it efficiently extract iridium(IV) [10], ruthenium(III) [11], and palladium(II) [12] from the hydrochloric acid solutions.

Table 1 lists the most informative chemical shifts in ^{13}C NMR spectrum of the compound L and its protonated form $(H_2L)Cl_2$ (dihydrochloride). The protonation resulted in broadening of all the signals, those of the 3,3' and 4,4' carbon atoms were simultaneously shifted upfield (the most pronounced shift was observed for the 4 and 4' atoms, adjacent to the amino groups), and the signals of the 1,1' and 2,2' carbon atoms (those at the amide groups) were shifted downfield. The spectral data pointed at protonation of the amine nitrogen atoms of compound L yielding the $(H_2L)Cl_2$ salt; the amide nitrogen atoms were not protonated. Therefore, it could be supposed that behavior of compound L under the extraction conditions would be similar to that of aliphatic amines.

In this work we used compound L in the dihydrochloride form $(H_2L)Cl_2$ (hereafter referred to as "reagent") as the extracting agent.

The optimal conditions of rhodium(III) extraction were found in the preliminary tests. The data in Fig. 1 showed that the distribution coefficient of rhodium(III) $D_{\mathrm{Rh(III)}} = c_{\mathrm{Rh(III),org}}/c_{\mathrm{Rh(III),aq}} = [c_{\mathrm{Rh(III),aq,0}} - c_{\mathrm{Rh(III),aq}}]/c_{\mathrm{Rh(III),aq}}$ upon the extraction with $(H_2L)Cl_2$ increased with the increasing concentration of hydrochloric acid over 0.5–2 mol/L range, owing to the accumulation of the extracted form $[RhCl_5(H_2O)]^{2-}$ [13]. Further increase of hydrochloric acid concentration (2–6 mol/L)

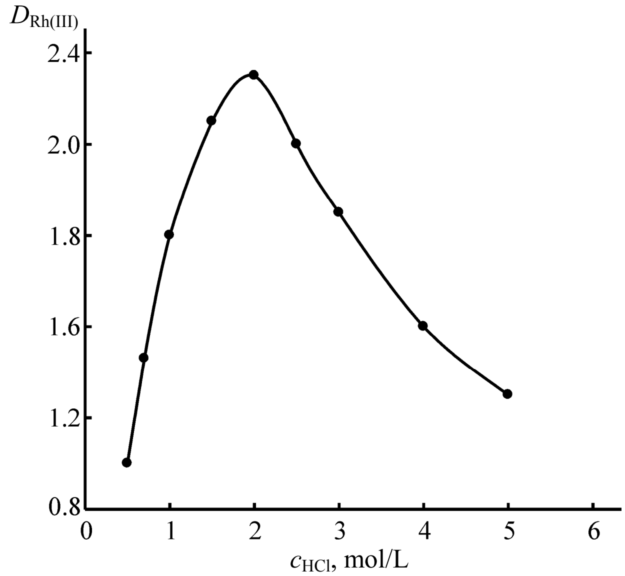


Fig. 1. The effect of hydrochloric acid concentration on the distribution coefficient of rhodium(III) $D_{Rh(III)}$. $c[(H_2L)Cl_2]$ = 0.023 mol/L, $c_{Rh(III)}$ = 0.002 mol/L, time of the phases contact 5 min.

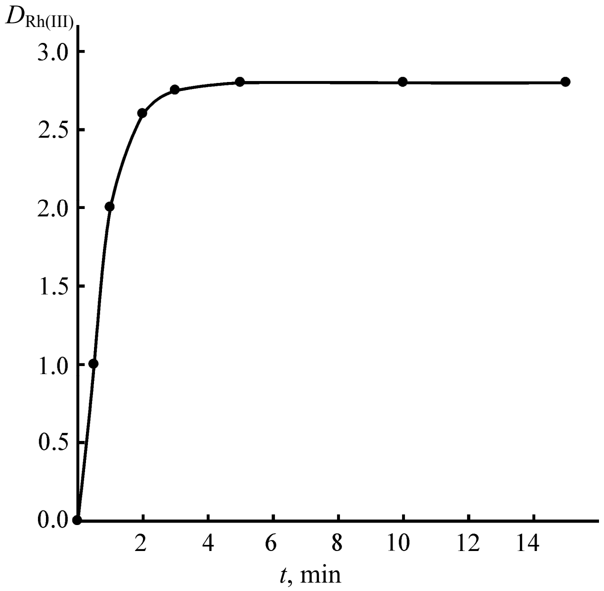


Fig. 2. The effect of time of the phases contact on the distribution coefficient of rhodium(III). $c[(H_2L)Cl_2]$ = 0.023 mol/L, $c_{Rh(III)}$ = 0.002 mol/L, c_{HCl} = 2 mol/L.

noticeably reduced the extraction degree of rhodium(III). Apparently, that was due to the accumulation of hardly extractable triply charged $RhCl_6^{3-}$ ions in a large excess of chloride ions. Kinetic studies revealed that the extraction equilibrium was established in no more than 5 min (Fig. 2); the high rate of the process pointing at the extraction of rhodium(III) via the interphace ion mechanism. Accounting for the discussed preliminary results, further extraction experiments were conducted at hydrochloric acid concentration of 2 mol/L and the phases contact time of 5 min.

Figure 3 shows the initial parts of isotherms of rhodium(III) extraction from the hydrochloric acid solutions. The steepness of the curves evidenced about efficient extraction of the metal ions. The solvate number q determined using the equilibrium shift method [14] equaled to unity (Fig. 4), thus revealing the formation of the extracted Rh(III) : L = 1 : 1 compound in the organic phase.

In order to elucidate the extraction mechanism, the extracted compound was isolated and characterized.

Table 1. Major parameters of ^{13}C NMR spectra of bisacylated triethylenetetramine L, its protonated form, and the Rh(III) extracted compound[a]

Compound	Parameter	Carbon atom			
		1,1'	2,2'	3,3'	4,4'
L	δ	179.72	39.73	48.65	52.74
$(H_2L)Cl_2$	δ_1	182.29	40.55	47.22	49.41
	Δ_1	2.57	0.82	–1.43	–3.33
$(H_2L)[RhCl_5(H_2O)]$	δ_2	182.43	41.13	48.52	50.11
	Δ_2	1.91	1.40	–0.13	–2.63
	δ_1–δ_2	–0.14	–0.58	–1.30	–1.00

[a] δ, δ_1, and δ_2, chemical shifts in the corresponding spectrum, ppm.; Δ_1 and Δ_2, changes of the chemical shifts compared to the spectrum of compound L.

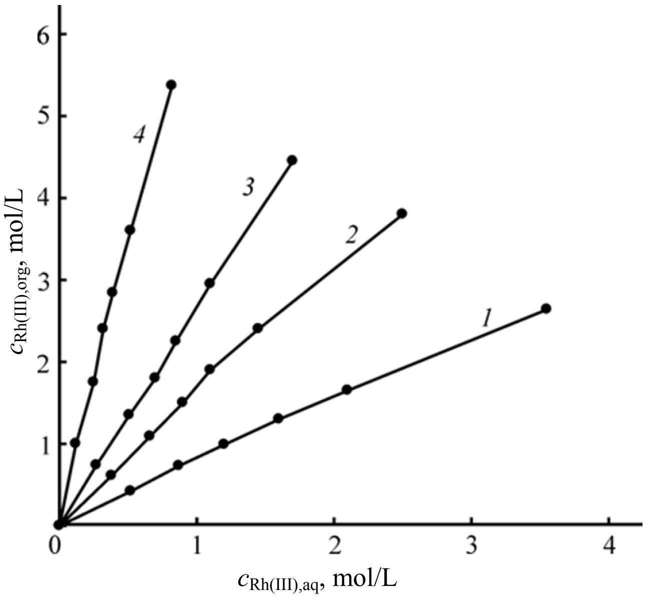


Fig. 3. The isotherms of extraction of rhodium(III) from hydrochloric acid solutions with the $(HCl)_2L$ reagent. T = 20°C, c_{HCl} = 2 mol/L; $c[(H_2L)Cl_2]$ = 0.012 (*1*), 0.023 (*2*), 0.035 (*3*), and 0.055 (*4*) mol/L; $c_{Rh(III),aq}$ and $c_{Rh(III),org}$, rhodium(III) concentrations in the aqueous and the organic phases, respectively.

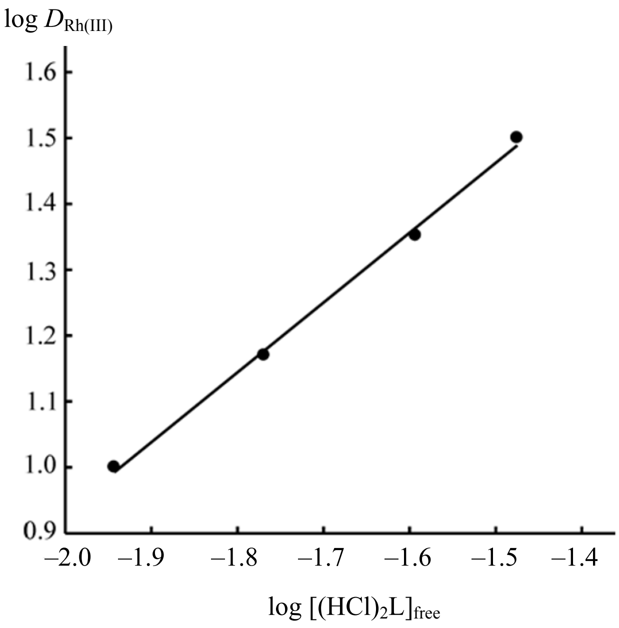


Fig. 4. The effect of concentration of the free reagent on rhodium(III) distribution coefficient. $c_{Rh(III)} = 2 \times 10^{-3}$ mol/L.

According to the elemental analysis, the n(Rh) : n(Cl) : n(N) ratio was of 1 : 5 : 4, corresponding to the $(H_2L)\cdot[RhCl_5(H_2O)]$ composition. Specific electrical conductivity of the compound solution in dry acetone (0.001 mol/L) determined via conductometry was of 160–165 Ω^{-1} cm^2 mol^{-1}, evidencing about rhodium(III) extraction in the form of ion associate.

Chemical shifts of carbon atoms of the extracted compound were marginally changed as compared to those in the spectrum of the extracting agent (Table 1). The upfield shift of the signals could be only assigned to substitution of the two chloride ions with pentachloroaquorhodate(III) ion; that confirmed the interphase anion exchange mechanism of the extraction.

Table 2. Major parameters of IR spectra (ν, cm^{-1}) of bis-acylated triethylenetetramine L, its protonated form, and the Rh(III) extracted compound

Assignment	L	$(H_2L)Cl_2$	$(H_2L)[RhCl_5(H_2O)]$
ν(C=O) (amide I)	1637 s	1624 m	1637 m
δ(H–O–H)			1620 m
δ(N–H) (amide II)	1533 s	1520 s	1524 m
$\delta(NH_2^+)$		2650 w	2660 w
ν(C–N)	1180 w	1180 w	1180 w
ν(Rh–O)			420 w
ν(Rh–Cl)			330 s, 322 s

Electronic absorption spectrum of the rhodium(III) extract in the visible spectral range was similar to that of the monomeric pentachloroaquarhodate(III) ion [13] and contained two absorption bands with maximums at 24500 cm^{-1} ($^1A_{1g}\rightarrow{}^1T_{1g}$) and 19800 cm^{-1} ($^1A_{1g}\rightarrow{}^1T_{2g}$).

Parameters of the major absorption bands in IR spectra of the studied compounds are listed in Table 2; the assignment was made using the information from [15–18]. Characteristic band of the ν(Rh–N) (530 cm^{-1}) was absent in the spectrum of the extracting compound, whereas the major absorption bands of amide and amine groups in the spectra of the extracting agent and the extracted compound were practically the same. Those spectral data evidenced that the metal ion was not coordinated with nitrogen atoms of the extracting agent. Strong absorption bands at 322 and 330 cm^{-1} in the spectrum of the extracted compound were assigned to the ν(Rh–Cl) {those bands were located at 335 and 326 cm^{-1} in the spectrum of the $[RhCl_5(H_2O)]^{2-}$ ion}.

The obtained spectral data suggested that rhodium(III) was extracted by the studied reagent via the interphase anion exchange according to Eq. (1).

the concentration constants of rhodium(III) extraction

$$(H_2L)Cl_{2,\text{org}} + [RhCl_5(H_2O)]^{2-}_{\text{aq}} \rightleftarrows (H_2L)[RhCl_5(H_2O)]_{\text{org}} + 2Cl^{-}_{\text{aq}}. \quad (1)$$

The concentration constant [mol/L] of rhodium(III) extraction in the studied system was expressed as follows.

$$K_{\text{conc}} = c_{\text{Rh(III),org}}[Cl^{-}]^2/c_{\text{Rh(III),aq}}\{c[(H_2L)Cl_2] - c_{\text{Rh(III),org}}\}. \quad (2)$$

In Eq. (2): $c_{\text{Rh(III),aq}}$ and $c_{\text{Rh(III),org}}$ are concentrations of rhodium(III) in the aqueous and the organic phases, respectively, and $c[(H_2L)Cl_2]$ is the total reagent concentration.

Mean value of the concentration constant of rhodium(III) extraction K_c was of 320±10 mol/L.

Comparison of the concentration constants of rhodium(III) extraction with the known nitrogen-containing agents (trioctylamine K_c = 20±1, Aliquat 336 K = 40±1 [19]) and that determined in this work revealed that the extraction ability of the $(H_2L)Cl_2$ agent was noticeably higher than the modern analogs.

As seen from Fig. 5, the effect of temperature on the distribution coefficient of rhodium(III) in the studied system was not significant, i.e., the extraction process was determined by both the entropy and the enthalpy factors. The $D_{\text{Rh(III)}}$ as function of temperature obeyed the Arrhenius law, enabling determination of thermodynamic parameters of extraction: ΔH^0 = –8.7±0.5 kJ/mol, ΔS^0 = 19.1±0.5 J mol^{-1} K^{-1}, and ΔG^0 = –14.3±0.5 kJ/mol.

Noteworthily, rhodium(III) could be readily back-extraction from the organic phase with hydrochloric acid solution (9 mol/L) or thiourea (5 wt % in 1 mol/L HCl). If the phases volumes were equal and their contact time was of 15 min, 90% of the extracted rhodium could be back-extraction in a single step.

To summarize, we demonstrated the efficiency of bisacylated triethylenetetramine dihydrochloride towards extraction of rhodium(III) from solutions of hydrochloric acid (0.5–4 mol/L). The extraction occurred via the interphase anion-exchange mechanism.

EXPERIMENTAL

Freshly prepared hydrochloric acid solutions of $K_2[RhCl_5\cdot(H_2O)]$ (in turn synthesized from “pure” grade $RhCl_3\cdot4H_2O$ as described elsewhere [20]) were used in this work. Hydrochloric acid of the “chemical pure” grade was used as well. Concentration of rhodium(III) in the stock solutions and the raffinates was determined by means of spectrophotometry in the presence of tin(II) chloride [21]; relative error of the determination was below 5%. Concentration of rhodium(III) in the extracts was calculated as the difference between those in the stock solution and the raffinate.

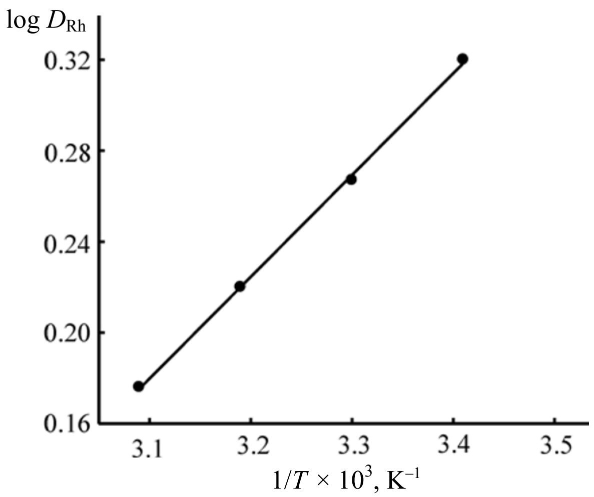


Fig. 5. Determination of thermodynamic parameters of Rh(III) extraction with $(H_2L)Cl_2$.

Bisacylated triethylenetetramine (L) was a light-brown viscous liquid, soluble in aromatic hydrocarbons, chloroform, and dichloroethane, and insoluble in water and alkanes.

Dihydrochloride $(H_2L)Cl_2$. 5.0 g of compound L was dissolved in 30 mL of a toluen–*n*-octanol mixture 15 vol % of the alcohol); the solution was stirred with 30 mL of hydrochloric acid solution (2 mol/L) during 15 min at 20°C. The formed salt was precipitated with hexane, filtered off, washed with hexane and dried. Yield 3.88 g (67.7%), light-yellow powder. Found, %: C 62.0; H 9.9; N 9.6; Cl 13.2. $C_{28}H_{58}N_4Cl_2O_2$ (M = 553.8). Calculated, %: C 60.8; H 10.5; N 10.1; Cl 12.7.

A mixture of toluene with *n*-octanol (15 vol % of the alcohol) was used as diluent for the dihydrochloride $(H_2L)Cl_2$. A stock solution of the reagent was prepared via dissolution of certain amount of the substance in the diluent; its concentration was then determined via potentiometric titration with 0.05 mol/L NaOH solution (an OR-211/1 pH-meter, combined glass electrode). Working solutions were prepared via dilution of the stock one.

Extracted rhodium(III) compound. The extractant solution was saturated with rhodium in contact with a $K_2[RhCl_5(H_2O)]$ solution (2 mol/L of

HCl). The formed extracted compound was precipitated and washed with hexane, and then dried at room temperature. The so obtained red-brown viscous liquid was soluble in common organic solvents except for alkanes. Found, %: C 43.80; H 7.80; N 7.91; Cl 23.30; Rh 12.6. $C_{28}H_{60}N_4RhCl_5O_3$ (M = 780.16). Calculated, %: C 43.07; H 7.69; N 7.18; Cl 22.71; Rh 13.19.

Extraction and back-extraction of rhodium(III) was performed using a constant-temperature cell (20±0.5°C, except for the experiment shown in Fig, 5) at the 1 : 1 volume ratio of the aqueous and the organic phases. The cell content was stirred using a magnetic bar. After the extraction, the phases were separated via centrifugation (2 min, 5500 rpm, a JANETZKI T5 centrifuge).

Electronic absorption spectra of solutions in the toluene–*n*-octanol mixture (15% of the alcohol) were recorded using a Specord M40 spectrophotometer. IR spectra of thin films were registered using a Specord M80 spectrophotometer at 4000–200 cm^{-1}. ^{13}C NMR spectra of solutions in $CDCl_3$ were obtained using a Bruker AM-300 spectrometer (300.13 MHz, JMOD mode and wideband proton decoupling, TMS as internal reference). Electrical conductivity of the extracted compound solution in anhydrous acetone was measured with an OK-102/1 (Radelkis) conductometer equipped with a bell-shaped platinum electrode.

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